Electronic structure and optical properties in ZnO:M(Co, Cd) Effect of band-gap variation

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ABSTRACT

ZnO doped with some transitions metals (ZnO:M) has several significant potential application. ZnO:Co is proposed to be used in advanced spintronic devices due to its high Curie temperature and large magnetic moments per transition metal. ZnO:Cd has potential applications in short-wavelength optoelectronic devices. This work focuses on an ab-initio study of the electronic and optical properties of ZnO:M doped with Co, and Cd. Theoretical calculations have been done with different computational codes, using the density functional theory (DFT) at the GGA and GGA+U level. The latter introduces a Hubbard term correction in the "d" levels of the Zn and Co. We used different supercells in order to have different realistic dilution levels which can be achieved in experiments. Doping effects on the features of the optical absorption are also studied and analysed in this work.

1. Introduction

Diluted magnetic semiconductors have attracted many attentions due to their spintronic and potential technological applications. Zinc oxide where some Zn atoms are replaced by transition metal ions is considered one of these interesting systems. ZnO is a wide band-gap semiconductor (3.4 eV) used in optoelectronic devices because its high optical transparency. Due to the fact that its optical and electric properties are not very stable at high temperatures [1] in some cases it is preferred to be used in n-type doping.

ZnO doped with Cobalt has been extensively studied experimentally due to its magnetic properties ([2] and references within). Its optical properties show a deformation of the features of the absorption close to the edge of the valence band maximum with increasing Cobalt concentration [3]. Its ferromagnetism at thin-film has been reported close to room temperature, although the origin of magnetic properties is currently controversial. The ZnO doped with cadmium atoms allows the band-gap narrowing of the system [4]. This happens because CdO has a smaller band-gap (2.3 eV) than ZnO (3.43 eV). This effect of the band-gap engineering is very important to design optoelectronic devices.

In this work we investigate the electronic structure of ZnO doped with Cobalt or Cadmium using the density functional theory (DFT), including in some cases on-site Coulomb correlation term, for different concentrations of cobalt and cadmium. After that, the theoretical absorption coefficient was obtained for all systems and studied the variation of the absorption for several concentrations of the dopants.

2. Theoretical approach

The theoretical calculations have been done using the density functional theory (DFT) as implemented in the plane-wave Vienna Ab-initio Simulation Package (VASP) [5]. Generalized gradient approximation (GGA) has been used with the Perdew–Burke–Ernzerhof (PBE) functional [6]. We used the default projector augmented waves (PAW) potentials [7]. The Zinc d-states in the potential were explicitly treated as valence states having in this case 12 electrons ($4s^2 3d^{10}$). For oxygen we used 6 electrons ($2s^2 2p^4$), for cobalt 9 electrons ($4s^1 3d^8$) and for cadmium 12 electrons ($5s^2 4d^{10}$).

ZnO has a wurtzite structure (B4) with consist of hexagonal Zn and O planes stacked alternatively along the c-axis and the atoms are fourfold coordinated. To describe the pure semiconductor we have used a plane-wave basis set with a 400 eV energy cutoff and the Brillouin Zone (BZ) was sampled using an $11\times11\times9$ Monkhorst-Pack (MP) grids including the Γ point in the calculation (MP–Γ). Full atomic relaxations were made using convergence parameters up to 0.01 eV/Å for atomic forces and less than 1 meV for the total energy.

In order to compare with realistic experimental dopant concentrations, we have modelled different wurtzite supercells as a result of substituting zinc atoms by cobalt or cadmium. The used cells have 24 ($1\times2\times3$), 48 ($2\times2\times3$) and 108 ($3\times3\times3$) atoms. The different metal concentrations have been detailed in Table 1. The 108 atom supercell converged with a $2\times2\times2$ MP–Γ grid, the 48 atom cell with a $6\times6\times3$ MP–Γ, and the 24 atom cell with an $8\times8\times4$ MP–Γ.

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Table 1
GGA+U band-gap variation with the concentration of the dopants. ZnO:Co spin-down values refer to the gap between states which can be identified as the corresponding of the host semiconductor.

%	ZnO:Cd (eV)	ZnO:Co spin-up (eV)	ZnO:Co spin-down (eV)
2	2.00	1.9	2.13
4	1.76	1.69	2.13
8	1.35	1.28	2.13
17	1.19	1.1	2.13

The calculations have been made in all cases at their equilibrium undoped lattice constants and then atomic relaxations for metal doped ZnO were made.

Standard DFT underestimate the band-gap. In this case an additional underestimation is produced because the hybridization between the Zn-d states and the p-oxygen states is not taken into account correctly [8]. In order to correct this fact, we have included the effects of an on-site Coulomb correlation (DFT+U) in the calculations [9]. The meaningful parameter U_{eff} used was evaluated by adjusting the zinc d-orbitals position to experimental results (7.5 eV below Fermi energy) [10]. The U_{eff} used for the cobalt d-states was 2.8 eV [11] and no U_{eff} was used for the cadmium atom.

For calculating the optical properties, the imaginary part of the dielectric function was obtained as the sum over independent transitions between Kohn–Sham states, as given by Fermi's golden rule. This method was implemented in the OPTIC code and it is described in [12]. Only interband and direct transitions are considered for the determination of the imaginary part of the dielectric function and local-field effects (i.e., the off-diagonal terms of the dielectric matrix) are neglected in this approximation. The real part of the dielectric tensor was obtained from the imaginary part by the Kramers–Krönig relations. To get a converged frequency-dependent dielectric tensor, the Brillouin zone was sampled using a $14\times14\times7$ MP–Γ grid for the higher concentrations of Co and Cd (8% and 17%) and 190 empty bands were used. A $12\times12\times6$ MP–Γ grid and 230 empty bands were used for the concentration of 4%. For the 1% we used a $10\times10\times10$ MP–Γ grid and 400 empty bands.

3. Results

3.1. Electronic properties

Calculations for the undoped system have been recently presented by our group elsewhere [13]. Results give geometrical parameters close to the experiments and other theoretical calculations [14]. The GGA gap was 0.81 eV in agreement with similar theoretical calculations [15–17]. In order to avoid the underestimation of the binding energy of the Zn-d semi-core states we have applied the aforementioned DFT+U methodology. Using the $U_{eff}=8.5$ eV, the calculated DFT+U band-gap raise to 2.13 eV, giving an underestimated band-gap value of 1.3 eV.

3.1.1. Cobalt doped ZnO

Cobalt doped ZnO, where the metal substitutes a zinc atom, has been studied for the 2%, 4%, 8% and 17% cobalt concentration using the supercells described above. Other theoretical works have been done for different concentrations using GGA [18,19], GGA+U [20,21], hybrid functionals [22,23] and a SIC method [24]. When U_{eff} is not used, band-gap values obtained theoretically for the different Co-metal concentrations are similar to the value obtained for the host semiconductor. Theoretical determinations of the band-gap values have been made between the states which can be identified as the corresponding states of the host semiconductor. We have observed that the d-states appear inside the semiconductor band-gap. The use of a $U_{eff}=2.8$ eV value for the cobalt changes completely the electronic structure. Cobalt empty states appear now inside the conduction band and the filled states inside the valence band.

For the spin-up polarization, Cobalt states hybridize with valence band states and for the spin-down Cobalt states determine the top of the valence band. We have observed a decrease of the band-gap in the spin-up from the 2% to the 17% Cobalt concentration. For the spin-down states, the host semiconductor band-gap and the relative position of the cobalt minority levels are almost unchanged with the cobalt concentration, as shown in Table 1. The main change affects the relative position between the spin-up and spin-down states. For 8% and 17% cobalt concentrations the minimum gap is given by the spin-up states, but for 2% and 4% cobalt concentrations the spin down determines the minimum gap. This fact affects the calculated optical spectra. In Fig. 1 we show the total (DOS) and projected (PDOS) density of states results after atomic relaxation for the different cobalt concentrations.

3.1.2. Cadmium doped ZnO.

For the ZnO:Cd system calculations at the same concentration levels are carried out as in cobalt cases. The inclusion of cadmium, an isoelectronic element with Zn, does not produce a spin-polarization result as in the cobalt case. The new levels introduced for the cadmium appear between 6 and 7 eV above the Fermi level and close to the Zn-d levels. In this case the use of a U_{eff} value for the metal has been avoided because the cadmium d-states positions don't appear inside the band-gap and the correction will only affect slightly the optical gap. The theoretical optical spectra will thus be corrected using a scissor operator. The PDOS results for the top valence band and bottom conduction band are similar to those of the undoped system being the main effect that the inclusion of cadmium produces, the decreasing of the band-gap for the doped systems with the cadmium concentration (see Table 1). These electronic features are shown in Fig. 2.

3.2. Optical properties.

As explained above, the band-gap of the pure host semiconductor was underestimated 1.3 eV. In order to obtain realistic absorption spectra, we have applied a shift to the conduction band of 1.3 eV with respect to the Fermi energy in all cases.

Figs. 3 and 4 show the absorption coefficients of ZnO doped with different concentrations of Co and Cd. Comparison of the effect of the two different dopants shows that for the case of Cd, the features of the absorption are very similar when we change the concentration. The main effect of the concentration is a shift of the absorption edge accounting for the reduction of the band-gap that we have previously seen in the electronic properties. The different features observed for the case of 17% concentration can be due to the interaction between the two cadmiums in the unit cell.

For the case with Co, the situation is more complex, since we observe not only a shift but a deformation of the features of the absorption. The energy of the minimum transition depends slightly on the concentration of Co, but that implies the differences we observe in the absorption edge around 3 eV in Fig. 4. These differences are due to the variation in the spin-up band-gap commented in Table 1. On the contrary, the differences at energies from 4 to 5 eV and from 5.2 to 8.5 eV are determined by transitions involving spin-down Co states. Specifically, the Co states affect mainly the absorption in this latter energy range, in which the main contribution is due to transitions from the spin-down valence states to the empty d-states and transitions from the occupied d-states to the conduction band (see Fig. 1). Thus, producing a significant increase in the absorption in the range of around 5.2 to 8.5 eV.

We would like to remark that in this work, the band-gap calculations are not an extrapolation of the optical absorption calculations. We obtain using first-principles ab-initio calculations the electronic band diagram and density of states and we found a decreasing in the electronic gap due to hybridization between the sp-d electrons of the

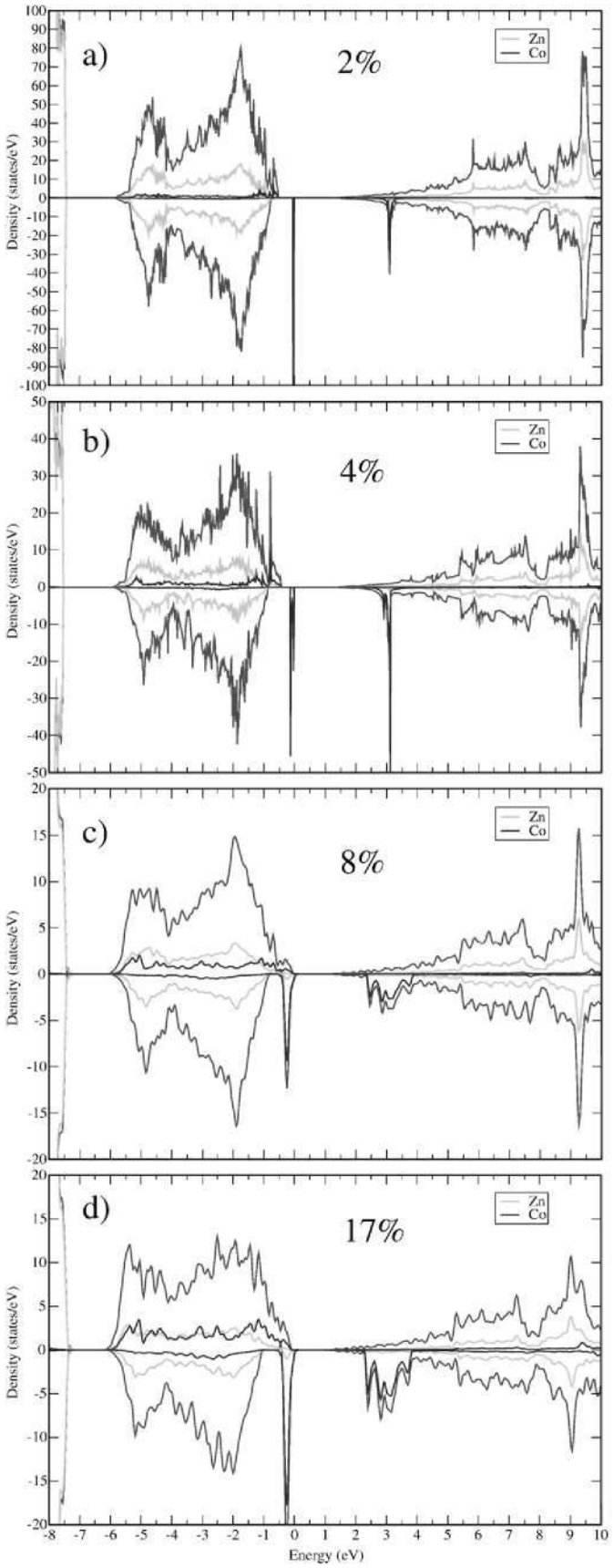

Fig. 1. Spin polarized total (DOS) and projected (PDOS) density of states for the Co-doped ZnO at different metal concentrations.

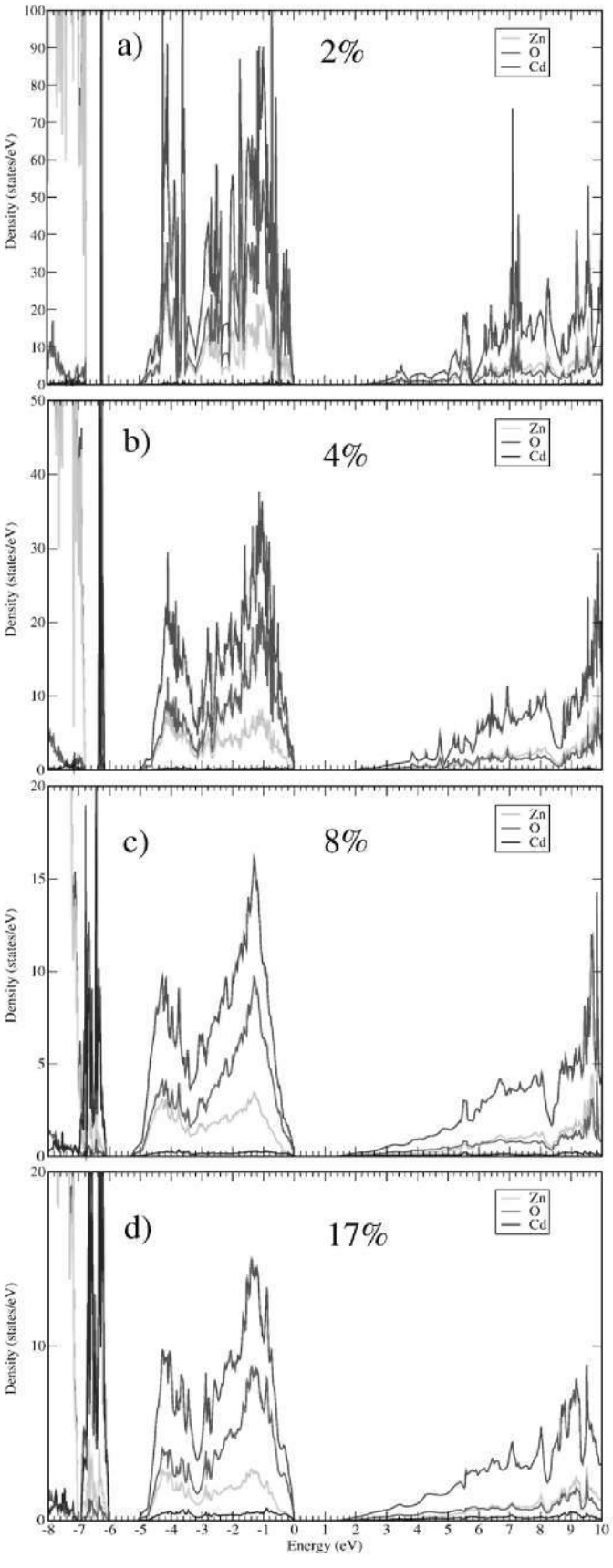

Fig. 2. Total (DOS) and projected (PDOS) density of states for the Cd-doped ZnO at metal concentrations.

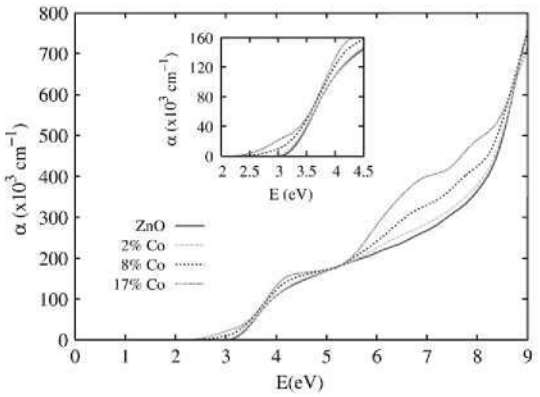

Fig. 3. Absorption coefficient of Co-doped ZnO at different metal concentrations. The inset shows an enlarged view of the plot.

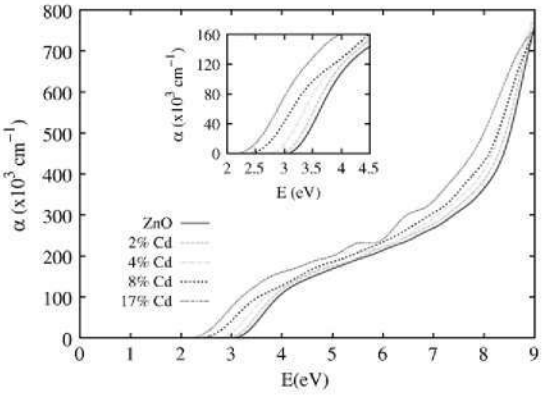

Fig. 4. Absorption coefficient of Cd-doped ZnO at different metal concentrations. The inset shows an enlarged view of the plot.

host semiconductor and d-electrons from the Co and Cd. This decreasing of the electronic band-gap is reproduced in the optical calculations obtained with the matrix elements of all the direct transitions between wavefunction eigenvalues.

4. Conclusions

The different behaviour of Co and Cd as dopants in ZnO has been studied from both the electronic and the optical point of view. Different concentrations of the dopants were represented in order to see how significant the effect of the metal is.

The influence of the inclusion of a Hubbard term was also discussed, being this term necessary to correct the position of the zinc and cobalt d-levels.

The main conclusions concerning the electronic behaviour are summarized in Table 1. The concentration of Cd reduces the gap of the semiconductor which makes it interesting for optoelectronic applications. The insertion of Co produces a reduction in the spin-up band-gap similar to cadmium doping, while the spin-down gap is preserved respect to the host semiconductor, even though the spin-down occupied d-states of the Co appear inside the semiconductor band-gap and the empty d-states appear hybridized with the conduction band.

The analysis of the optical absorption coefficient has shown that the concentration of Cd can only affect the absorption edge while the main features of the spectra are retained. These results are in concordance with experimental measurements [4].

On the contrary, the concentration of Co produces not only a reduction of the energy of the lowest allowed transition as Cd doping does, but a deformation of the features of the absorption at low energies with the increasing of Co concentration as observed in some experimental works [3]. Moreover a significant increase in the absorption in two energy ranges, from 4 to 5 eV and from 5.2 to 8.5 eV, with respect to the pure semiconductor is observed. These behaviours have to be taken into account when using these compounds for optoelectronic devices.

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